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Tool steel with reinforced tenacity, manufacturing process of parts in this steel and parts obtained.

The present invention relates to a composition of tool steel having a reinforced tenacity compared to the nuances of former art, a process of development of this composition as well as the parts which can be thus obtained.

The tool steels are very largely used in many applications in particular implying relative displacements between metal parts in contact, where one of the parts must preserve sound geometrical integrity longest possible. One can quote as examples of realization, the tools of machining and cut as well as the metrological equipment.

The conservation of the geometrical integrity of these parts requires a good wear resistance, a good strength to the deformation and breaking under requests static or dynamic, which implies that steel used has a high tenacity and a hardness.

In addition, the nuance must have a good hardenability, so that the structure is most homogeneous possible on great thicknesses after hardening.

However these various requirements appear very often contradictory.

Thus, one cold knows a nuance of tool steel for work called AJSI D2 and largely widespread, containing 1,5% in carbon weight and chromium 12% with some additions complementary to carbide-forming elements hardening such as Mo or V. The strong percentages of carbon and chromium lead to an important eutectic carbide precipitation of < type; RTI ID=1.1> M7C3< /RTI> who are trained at high temperature at the end of the solidification and coarse and are consequently divided in a heterogeneous way in the metal matrix.

If the presence of a large voluminal fraction of hard metals in steel is favorable to the reinforcement of the behaviour to wear, their bad distribution harms as for it tenacity.

To mitigate this problem, it < RTI ID=2.1> a< /RTI> then proposed to reduce the percentages of carbon and chromium of this type of nuances to respective contents of approximately 1 and 8% with in compensation a higher content molybdenum, about 2,5% (EP 0.930.374). The reduction of the percentage of carbon makes it possible to reduce the voluminal fraction of eutectic carbides what is favorable for tenacity. The enrichment of these carbides out of molybdenum which increases their hardness, makes it possible in its turn to maintain the hardness of steel and its behaviour with wear.

However, there would remain necessary to still refine the distribution of these carbides to increase tenacity without reducing the characteristics of hardness and behaviour to the wear of steel.

The inventors noted that a new improvement of the mechanical compromise tenacity-behaviour and with wear results in an unexpected way of a sufficient content nitrogen accompanied by a minimal content titanium and/or zirconium, itself function of the nitrogen content.

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More precisely, it was observed a refinement of carbides of chromium, molybdenum and tungsten, and a joint reinforcement of tenacity, when: - on the one hand NR < RTI ID=2.2> < /RTI> 0,004%, preferably < RTI ID=2.3> < /RTI> 0,006%, - in addition (Ti + Zr/2) X NR < RTI ID=2.4> < /RTI> 2,5.104% 2, Ti contents, Zr and NR being expressed in % ponderal.

This joint requirement nitrogenizes some and titanium or zirconium suggests that the active factor is the presence of zirconium and or titanium nitrides, supposed to play the part of refiner of the size of tungsten and molybdenum, chromium carbides. The average size of large tungsten and molybdenum, chromium carbides passes thus from a typical value from approximately 10 um according to former art, with a value of approximately < RTI ID=2.5> 4< /RTI> um, according to the present invention.

A first object of the invention is thus consisted a steel whose composition includes/understands, the percentages being expressed in % in weight:

0,8 < RTI ID=2.6> < /RTI> < RTI ID=2.7> C< /RTI> < RTI ID=2.8> < /RTI> 1,5

5,0 < Cr < 14 < RTI ID=2.9> 0, 2 Mn< /RTI> 3

Nor < < RTI ID=2.10> 5< /RTI>

V < RTI ID=2.11> < /RTI> 1

Nb < RTI ID=3.1> zig< /RTI> 0,1 < RTI ID=3.2> Si+Al< /RTI> < 2 < RTI ID=3.3> Cu #< /RTI> < RTI ID=3.4>

S< /RTI> < RTI ID=3.5> #< /RTI> 0,3

Ca < RTI ID=3.6> < 0, < /RTI> 1

< RTI ID=3.7> # 0,1< /RTI>

Te < RTI ID=3.8> < 0, < /RTI> 1

1,0 < RTI ID=3.9> # Mo+W/2 #< /RTI> 4

0,06 < RTI ID=3.10> < < /RTI> Ti+Zr/2 < RTI ID=3.11> # 0, < /RTI> 15
 0,004 < RTI ID=3.12> < NR < < /RTI> 0,02 the remainder of the composition making up of iron and impurities
 resulting from < RTI ID=3.13> lelaboration, < /RTI> moreover being understood that < RTI ID=3.14> : 2, < /RTI> 5.
 10-4 < RTI ID=3.15> %2 # < /RTI> (Ti + < RTI ID=3.16> Zr/2) < /RTI> X NR.

In a mode of realization preferred of the invention, the composition of steel includes/understands, the percentages being expressed in % in weight:

0,8 < RTI ID=3.17> < < /RTI> C < RTI ID=3.18> < < /RTI> 1,2

7,0 < Cr < 9

0,2 < RTI ID=3.19> < Mn < < /RTI> 1,5 < RTI ID=3.20> # < /RTI>

0,1 < < RTI ID=3.21> V # < /RTI> 0,6

Nb < RTI ID=3.22> # 0, < /RTI> 1

Si+Al < RTI ID=3.23> # 1, < /RTI> 2 < RTI ID=3.24> Cu # 1</RTI> < RTI ID=3.25> s< /RTI> 0,3

Ca < RTI ID=3.26> zu< /RTI> 0, 1

< RTI ID=3.27> # 0, < /RTI> 1

Te < 0,1

2,4 Mo+W/2 3

0,06 < RTI ID=3.28> # Ti+Zr/2 # < /RTI> 0,15

0, < RTI ID=3.29> 004 # NR # < /RTI> 0,02 the remainder of the composition making up of iron and impurities
 resulting from the development, moreover being understood that < RTI ID=4.1> : 2, < /RTI> 5.10- 4% 2 < (Ti + < RTI
 ID=4.2> Zr/2) < /RTI> X NR.

The content of titanium and/or zirconium of steel according to the invention must lie between 0,06 and 0,15% in weight. Indeed, beyond 0,15% in weight, the titanium nitride precipitation < RTI ID=4.3> et/ou< /RTI> of zirconium tends to coalesce and lose of its effectiveness. On the other hand, if the content is lower than 0,06% in weight, quantity of titanium < RTI ID=4.4> et/ou< /RTI> of zirconium present is insufficient to form sufficient zirconium and/or titanium nitrides to obtain the improvement sought in tenacity and wear resistance. It will be noted that zirconium can be substituted in whole or part for titanium in the proportion of two zirconium shares for a titanium share.

The nitrogen content of steel according to the invention must lie between 0,004 and 0,02% in weight, preferably between 0,006 and 0,02% in weight. One limits his content to 0,02% of weight bus beyond, tenacity tends to decrease.

The percentage of carbon of steel according to the invention must lie between 0,8 and 1,5% in weight, preferably between 0,8 and 1,2% in weight. Carbon must be present in a sufficient quantity to form carbides and to reach the level of hardness which one wishes to obtain for the nuance.

In another mode of realization preferred, the percentage of carbon of steel according to the invention is included/understood between 0,9% and 1,5% of weight, in order to ensure an improved hardness, with unchanged heat treatment, and to reinforce the behaviour with wear by increasing the voluminal fraction of hard metals.

The chromium content of steel according to the invention must lie between 5 and 14% in weight, preferably between 7 and 9% in weight. This element makes it possible on the one hand to increase the hardenability of the nuance and, on the other hand, to form hardening carbides.

The manganese content of steel according to the invention must lie between 0,2 and 3% in weight, preferably between 0,2 and 1,5% in weight. One adds it in the nuance according to the invention because it is a soaking element, but one limits his content to limit the segregation which would involve a bad forgeability and a too low tenacity.

Steel can contain up to 5% in nickel weight. Preferably, the content of this element must remain lower than 1% in weight. One can add it in the nuance according to the invention because it is a soaking element and which does not pose a problem of segregation. His content however is limited because it is an element gammagene favorable to the residual austenite formation.

To reinforce resistance to softening in the frequent case where steel is subjected to income before use, it is useful to add to the composition of the elements < RTI ID=5.1> carburigènes< /RTI> strong formant with the income of fine carbides of the < types; RTI ID=5.2> MC.< /RTI>

Among them vanadium is preferred, and one then uses it in contents from at least 0,1% but not exceeding < RTI ID=5.3> 1%, préférentiellement< /RTI> lower than 0,6%.

The niobium, which tends to precipitate at higher temperature and which, so night < RTI ID=5.4> strongly with the forgeabilité< /RTI> steel is to be avoided and will not exceed in any case 0,1%, and will be preferably lower than 0,02% in weight.

The content of silicon and/or aluminium of steel according to the invention must be lower than 2% in weight. In addition to their role of deoxidation of the nuance, these elements make it possible to slow down the coalescence of carbides in temperature and reduce of this fact your kinetics of softening to the income. One limits their content bus beyond 2% of weight, they weaken the nuance.

The content of molybdenum and/or tungsten of steel according to the invention must lie between 1 and 4% in weight, preferably between 2,4 and 3% in weight. It will be noted that tungsten can be substituted in whole or part for molybdenum in the proportion of two tungsten shares for a molybdenum share. These two elements make it possible to improve the hardenability of the nuance and to form hardening carbides. Their content is limited because they are at the origin of segregations.

Copper can be present in steel in content nevertheless lower than < RTI ID=5.5> 1%< /RTI> not to harm the forgeability of the nuance.

In addition, in order to improve < RTI ID=5.6> the usinabilité< /RTI> steel, sulphur, in a content not exceeding 0,3% can be added, possibly accompanied by calcium, selenium, tellurium in contents each one lower than 0,1%.

The development of the nuance of steel according to the invention, including the mode of addition of titanium and/or zirconium, can be done by very proceeded traditional, but can be carried out in an advantageous way by the process according to the invention which constitutes a second object of the invention.

This manufacturing process of parts includes/understands a first stage consisting in working out molten steel by fusion of the whole of the elements of the nuance according to the invention, except for titanium and/or of zirconium, then to add to the crucible cast steel bath titanium and/or zirconium by at any moment avoiding the local titanium < over-concentrations; RTI ID=6.1> et/ou< /RTI> out of zirconium in the crucible cast steel bath.

Indeed, these inventors noted that the traditional processes of addition, according to < RTI ID=6.2> the art< /RTI> former, of titanium and zirconium in the form of ferro-alloy solid elements or metal, generated zirconium and/or titanium nitrides coarse and consequently fewer, < RTI ID=6.3> of as much plus that then une< /RTI> partie d'entre eux peuvent < RTI ID=6.4> même décanter. Cette< /RTI> situation seems to be to connect to the fact that these processes of addition cause strong local zirconium and/or titanium over-concentrations in the liquid in the vicinity of the added elements.

One of the modes of realization of this first stage of the process according to the invention consists in adding titanium < RTI ID=6.5> et/ou< /RTI> zirconium in the slag covering the molten steel bath continuously, titanium and/or zirconium then spreading in a progressive way in the steel bath.

Another mode of realization of this first stage of the process according to the invention consists in adding titanium < RTI ID=6.6> et/ou< /RTI> zirconium by continuously introducing a wire made up of this or these elements into the crucible cast steel bath, while agitating the bath by bullage or any other adapted process.

Another mode of realization of this first stage of the process according to the invention consists in adding titanium and/or zirconium into blowing a powder containing this or these elements in the crucible cast steel bath, while agitating the bath by bullage or any other adapted process.

Within the framework of this invention, one prefers to use the various modes of realization which have been just described, but it that very is clearly understood proceeded making it possible to avoid a local over-concentration out of titanium and/or out of zirconium could be put in < RTI ID=6.7> oeuvre.< /RTI>

The development is generally carried out in a light-arc furnace, or an induction furnace.

With the exit of this development, molten steel is run in ingots or slabs. In order to refine his structure, one will be able to carry out a mixing in the ingot mould or even to use the process of remelting under slag with consumable electrode.

These ingots or these slabs are then transformed by means of treatments of working by plastic deformation hot adapted such as forging or rolling, for example.

Steel can then be subjected to a heat treatment according to traditional ways' for steels of tools. Such a heat treatment can possibly comprise an annealing to facilitate cutting and machining, then < RTI ID=7.1> a austénitisation< /RTI> followed by a cooling according to a mode adapted to the thickness, < RTI ID=7.2> small fireclay cup that a-cooling has to you air or àj' huite, possibly sdvi de< /RTI> incomes according to the level of hardness that < RTI ID=7.3> one < /RTI> souhaite atteindre.

A third object of the invention is consisted a steel part of composition in conformity with the invention or obtained by the implementation of the process according to the invention and whose average size of tungsten or molybdenum, the chromium carbide precipitates of resulting from solidification lies between 2,5 and 6 < RTI ID=7.4> um, < /RTI> preferably between 3 and < RTI ID=7.5> 4, < /RTI> < RTI ID=7.6> 5< /RTI> um.

The present invention is illustrated starting from the observations and of the following examples, table 1 giving the chemical composition of steels tested, among which casting < RTI ID=7.7> 1< /RTI> is in conformity with the present invention, while casting 2 is given as comparison.

EMI7.1

```
< composition; SEP> Run < SEP> 1 < SEP> Run < SEP> 2
< tb> (% < SEP> in < SEP> weight)
< tb> < SEP> C< SEP> 0, < SEP> 98 < SEP> 0, < SEP> 96
< tb> < SEP> Cr < SEP> 8, < SEP> 40 < SEP> 8, < SEP> 20
< tb> < SEP> Mn < SEP> 0, < SEP> 79 < SEP> 0, < SEP> 83
< tb> < SEP> Nor < SEP> 0, < SEP> 35 < SEP> 0, < SEP> 31
< tb> < SEP> Cu < SEP> 0, < SEP> 26 < SEP> 0, < SEP> 22
< tb> < SEP> V < SEP> 0, < SEP> 37 < SEP> 0, < SEP> 40
< tb> < SEP> Nb < SEP> 0, < SEP> 01 < SEP> 0, < SEP> 09
< tb> < SEP> If < SEP> 0, < SEP> 97 < SEP> 0, < SEP> 94
< tb>
```

EMI8.1

```
< tb> Al < SEP> 0, < SEP> 03 < SEP> 0,03
< tb> Mo < SEP> 2, < SEP> 60 < SEP> 2, < SEP> 50
< tb> < SEP> W < SEP> ~
< tb> Ti < SEP> 0, < SEP> 11 < SEP> 0,004
< tb> Zur
< tb> < SEP> 0, < SEP> 011 < SEP> 0, < SEP> 009
< tb>
```

Abbreviations employed

Pv : voluminal loss, expressed in < RTI ID=8.1> mm3, < /RTI>

Kv: energy of rupture, expressed in J/cm2,

T: tenacity, expressed in $\langle \text{RTI ID}=8.2 \rangle \text{ J/cm}^2 \cdot \langle \text{RTI} \rangle$

1-Tenacity example

One manufactures two parts starting from casting 1 in conformity with the invention and of comparative casting 2, while hot rolling with $\langle \text{RTI ID}=8.3 \rangle 1150 \text{ C} \cdot \langle \text{RTI} \rangle$ ingots worked out in these compositions. The samples are then austénitisés with $\langle \text{RTI ID}=8.4 \rangle 1050 \text{ C} \cdot \langle \text{RTI} \rangle$ during one hour, soaked with the oil then subjected to a double income of 525 C during one hour to obtain a hardness of 60 Hrc.

One proceeds then to two series of test using of the different methods to measure tenacity: - a deflection test per shock on Charpy test-tube taking the shape of a bar notched out of V according to the standard NF INTO 10045-2, which provides the energy of rupture Kv and $\langle \text{RTI ID}=8.5 \rangle - \text{un} \cdot \langle \text{RTI} \rangle$ deflection test per shock on bar not notched (bar of 10mm on 10mm), which provides tenacity T.

The results obtained are gathered in the following table:

EMI8.2

$\langle \text{SEP} \rangle \text{ Kv} \cdot \langle \text{SEP} \rangle \text{ T}$
$\langle \text{tb} \rangle \cdot \langle \text{SEP} \rangle (\text{J/cm}^2) \cdot \langle \text{SEP} \rangle (\text{J/cm}^2)$
$\langle \text{tb} \rangle \text{ Run} \cdot \langle \text{SEP} \rangle 1 \cdot \langle \text{SEP} \rangle 14, \cdot \langle \text{SEP} \rangle 0 \cdot \langle \text{SEP} \rangle 59$
$\langle \text{tb} \rangle \text{ Coulée2} \cdot \langle \text{SEP} \rangle 10, \cdot \langle \text{SEP} \rangle 5 \cdot \langle \text{SEP} \rangle 47$
$\langle \text{tb} \rangle$

On voit que, quelle que soit la méthode employée, la coulée 1 selon l'invention présente une ténacité améliorée par rapport à la coulée 2 comparative.

2-Resistance example to wear

One manufactures two parts in a way similar to that used in example 1, and one carries out a measurement of the wear resistance while following the standard $\langle \text{RTI ID}=9.1 \rangle \text{ ASTM} \cdot \langle \text{RTI} \rangle \text{ G52}$ which makes it possible to determine the voluminal loss undergone by the samples tested. This test consists in measuring the loss of weight of the sample subjected to the abrasive wear of a quartzic sand net with granulometry gauged introduced between a rubber wheel and the fixed sample.

The results obtained are gathered in the following table:

EMI9.1

$\langle \text{SEP} \rangle \text{ Statement}$
$\langle \text{tb} \rangle \cdot \langle \text{SEP} \rangle (\text{mm}^3)$
$\langle \text{tb} \rangle \text{ Coulée1} \cdot \langle \text{SEP} \rangle 17, \cdot \langle \text{SEP} \rangle 5$
$\langle \text{tb} \rangle \text{ Coulée2} \cdot \langle \text{SEP} \rangle 18, \cdot \langle \text{SEP} \rangle 5$
$\langle \text{tb} \rangle$

On constate que la coulée 1 selon l'invention présente une résistance à l'usure légèrement améliorée par rapport à la coulée 2 comparative.

CLAIMS :

1. Tooling steel with a composition comprising the following, the percentages being expressed as % by weight:

$$0.8 \leq C \leq 1.5$$

$$5.0 \leq Cr \leq 14$$

$$0.2 \leq Mn \leq 3$$

$$Ni \leq 5$$

$$V \leq 1$$

$$Nb \leq 0.1$$

$$Si+Al \leq 2$$

$$Cu \leq 1$$

$$S \leq 0.3$$

$$Ca \leq 0.1$$

$$Se \leq 0.1$$

$$Te \leq 0.1$$

$$1.0 \leq Mo+W/2 \leq 4$$

$$0.06 \leq Ti+Zr/2 \leq 0.15$$

$$0.004 \leq N \leq 0.02$$

the rest of the composition being made up of iron and foreign matter resulting from the processing, and further it is understood that: $2.5 \times 10^{-4} \%^2 \leq (Ti + Zr/2) \times N$.

2. Steel according to Claim 1, characterised in addition in that the composition comprises the following, the percentages being expressed as % by weight:

$$0.8 \leq C \leq 1.2$$

$$7.0 \leq Cr \leq 9$$

$$0.2 \leq Mn \leq 1.5$$

$$Ni \leq 1$$

$$0.1 \leq V \leq 0.6$$

$$Nb \leq 0.1$$

$$Si+Al \leq 1.2$$

$$Cu \leq 1$$

$$S \leq 0.3$$

$$Ca \leq 0.1$$

$$Se \leq 0.1$$

$$Te \leq 0.1$$

$$2.4 \leq Mo+W/2 \leq 3$$

$$0.06 \leq Ti+Zr/2 \leq 0.15$$

$$0.004 \leq N \leq 0.02$$

the rest of the composition being made up of iron and foreign matter resulting from the processing, and further it is understood that: $2.5 \times 10^{-4} \%^2 \leq (Ti + Zr/2) \times N$.

3. Steel according to Claim 1 or 2, further characterised in that the niobium content is below or equal to 0.02% by weight.

4. Steel according to any one of the Claims 1 to 3, characterised further in that the nitrogen content is between 0.006 and 0.02% by weight inclusive.

5. Process for manufacturing a steel component with a composition according to any one of the Claims 1 to 4, characterised in that

- a liquid steel is worked by melting all of the elements of the said composition, with the exception of the titanium and/or zirconium, then the titanium and/or zirconium is added to the melted steel bath while avoiding at any time local overconcentrations of titanium and/or zirconium in the melted steel bath;

- the said liquid steel is poured to make an ingot or a slab;

- the said ingot or slab is subjected to a forming treatment by hot plastic deformation, then possibly to heat treatment to make the said component.

6. Process according to Claim 5, characterised in that the titanium and/or zirconium are added continuously into a slag covering the bath of liquid steel, the titanium and/or zirconium then spreading out gradually in the said steel bath.

7. Process according to Claim 5, characterised in that the titanium and/or zirconium are added by continuous introduction of a titanium and/or zirconium wire into the steel bath, while the said bath is being stirred.

8. Process according to Claim 5, characterised in that the titanium and/or zirconium are added by blowing a powder containing the titanium and/or zirconium into the melted steel bath, while the bath is being stirred.

9. Steel component with a composition in accordance with any one of the Claims 1 to 4 or made by using the process according to any one of the Claims 5 to 8, characterised in that the

average size of the precipitates of molybdenum or tungsten or chromium carbides from the solidification is between 2.5 and 6 μm .

10. Steel component according to Claim 9, characterised further in that the average size of the molybdenum or tungsten or chromium carbides from the solidification is between 3 and 4.5 μm .